

## SPECIFICATION

## NANOCARBON PRODUCING APPARATUS

## 5 TECHNICAL FIELD

The present invention relates to a nanocarbon producing apparatus.

## BACKGROUND ART

10 Recently technological application of nanocarbon is actively studied. The nanocarbon means a carbon substance having a nanoscale fine structure, typified by a carbon nanotube, a carbon nanohorn, and the like. Among others, the carbon nanohorn has a tubular structure in which one end of the carbon nanotube formed by a cylindrically  
15 rounded graphite sheet is formed in a circular conic shape. Usually the carbon nanohorns aggregate in a form, in which the circular conic unit is projected from a surface like a horn while the tube is located in the center by Van der Waals force acting between circular conic units. The carbon nanohorn assembly is expected to be applied to  
20 various technical fields due to specific characteristics thereof.

It is reported that the carbon nanohorn assembly is produced by a laser vaporization method of irradiating the carbon substance (hereinafter also referred to as "graphite target") of a raw material with a laser beam in an inert gas atmosphere (Patent Document 1).  
25 In Patent Document 1, a CO<sub>2</sub> gas laser is illustrated as the laser beam.

The CO<sub>2</sub> gas laser has a wavelength of about 10.6  $\mu\text{m}$ , and ZnSe

and the like are preferably used as a material which transmits the CO<sub>2</sub> gas laser (Patent Document 2). Therefore, in producing the carbon nanohorn assembly with the CO<sub>2</sub> gas laser, it is considered that the laser beam can be focused on a surface of the graphite target by using  
5 the ZnSe lens.

[Patent Document 1] Japanese Laid-open patent publication NO.  
2001-64004

[Patent Document 2] Japanese Laid-open patent publication NO.  
2001-51191

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#### DISCLOSURE OF THE INVENTION

The invention studies the method of producing the carbon nanohorn assembly by providing a window made of ZnSe (also referred  
15 to as "laser beam window") in a producing chamber. Then, it is found that a weight ratio (hereinafter referred to as "yield") of the carbon nanohorn assembly is decreased in a recovered soot-like substance as an operating time of the laser beam window is lengthened. A lifetime of the laser beam window is relatively shorter, and sometimes the  
20 laser beam window failed. As a result, it is found that the apparatus is expensive to maintain and the lifetime of the apparatus becomes shorter. For the ZnSe lens provided outside the chamber, the lifetime is also relatively shorter.

Therefore, the reason why the yield of the carbon nanohorn  
25 assembly is decreased and the reason why the lifetime of the laser beam window or the lens is short are studied. As a result, in irradiating the graphite target with the laser beam, the soot-like

substance created from carbon vapor generated from the graphite target adheres to a surface of the laser beam window, and it is found that the adhesive soot-like substance is a possible cause of the reasons. When the soot-like substance adheres to the surface of the laser beam window or the lens, it is also clear that the laser beam window or the lens is heated by generating light absorption in the portion to which the soot-like substance adheres.

In such cases, there is a possibility that an optical path is shifted by a thermal lens effect. The shift of the optical path may shift a radiation position of the CO<sub>2</sub> gas laser in the surface of the graphite target or cause a change in power density of the light with which the surface is irradiated. It is speculated that this is the reason why the yield is decreased as the operating time of the apparatus is increased. Further, it is speculated that the heating of the laser beam window or the lens causes the failure and the like. Therefore, the technology in which the carbon nanohorn assembly is produced without decreasing the yield of the carbon nanohorn assembly is required. In order to lengthen the apparatus lifetime, the technology different from the conventional technology is required.

The present invention is performed in view of the foregoing circumstances, an object of the invention is to provide a technology in which the nanocarbon is stably obtained at high yield. Another object of the invention is to provide a technology in which the lifetime of the nanocarbon producing apparatus is lengthened.

The inventor actively has studied on a technique of obtaining the nanocarbon at high yield. As a result of that study, the inventor finds it important that the optical member is shielded from the adhesion

of the soot-like substance when the graphite target surface is irradiated with the light outgoing from a light source using the optical members, and the inventor reaches the invention. Further, the inventor finds that the optical member is protected from the adhesion of the soot-like substance by not directly irradiating the graphite target surface with the light outgoing from the light source, but by irradiating the graphite target after the light is reflected to change the optical path, and the inventor reaches the invention.

According to the invention, there is provided a nanocarbon producing apparatus characterized by including a graphite target; a chamber which accommodates the graphite target; a window unit which is provided in a part of the chamber; a light source which irradiates light onto a surface of the graphite target through the window unit; a recovery unit which recovers a nanocarbon generated from carbon vapor, the carbon vapor being vaporized from the graphite target by the light irradiation; and a shielding member which is located between the window unit and the graphite target.

In the invention, the shielding member is provided between the window unit and the graphite target. As described above, in the case of the configuration in which the surface of the graphite target is directly irradiated with the light after the light outgoing from the light source is transmitted through the window unit, the soot-like substance obtained from the carbon vapor generated from the surface of the graphite target also flies in a direction in which the soot-like substance returns to the window unit side, so that the soot-like substance is easy to adhere to the surface of the window unit. Therefore, in the case where the optical member made of ZnSe is used,

the optical member is easy to be heated.

On the contrary, in the configuration of the invention, the window unit is configured to be shielded from the surface of the graphite target. Therefore, even if the soot-like substance generated from the surface of the graphite target flies onto the window unit side, since the window unit is shielded by the shielding member, the soot-like substance which is moved toward the window unit to adhere to the surface thereof is suppressed. Accordingly, the power density of the light with which the graphite target is irradiated can be stabilized to stably produce the nanocarbon having the desired property at high yield.

In the invention, the shielding member is arranged such that the window unit is shrouded against the carbon vapor vaporized from the graphite target. The shielding member can be configured to keep the window unit shrouded so as not to adhere the soot-like substance obtained by the carbon vapor generated from the graphite target surface while causing the light outgoing from the light source to reach the graphite target surface.

In the invention, the chamber accommodates the graphite target. However, the whole of the graphite target may not be accommodated. A part of the graphite target may be accommodated.

In the invention, the window unit is the optical member which transmits the light outgoing from the light source. For example, the laser beam window or the lens and the like can be used as the window unit. The window unit is arranged while a part of the window unit is exposed to the inside of the chamber. The window unit may be arranged in an outgoing end face of the light source or the like

in the form of a part of the light source, or arranged in a wall surface of the chamber, in which the graphite target is accommodated, in the form of the member independent of the light source.

In this specification, the term "power density" means the power  
5 density of the light with which the graphite target surface is actually irradiated, namely, the power density at a radiation region of the light in the graphite target surface.

In a nanocarbon producing apparatus of the invention, an optical member for introducing the light to the surface of the graphite target  
10 may be included between the window unit and the shielding member. Therefore, the graphite target surface can securely be irradiated with the light, which allows the nanocarbon to be stably produced. In the invention, since the shielding member is provided between the optical member and the graphite target, the soot-like substance which  
15 flies in the direction of the window unit without recovering by the recovery unit to adhere to the surface of the optical member can be suppressed. Therefore, the radiation position shift of the laser beam in the graphite target surface caused by the thermal lens effect or the fluctuation in power density of the light in the surface can  
20 be suppressed, which allows the nanocarbon having the desired property to be produced stably and continuously. Accordingly, the yield of the nanocarbon can be improved. Since the heating of the optical member is suppressed, the failure of the optical member can be suppressed to lengthen the lifetime of the optical member. The  
25 increase in maintenance cost of the apparatus due to exchange of the optical members can be suppressed. Therefore, the apparatus configuration having the excellent endurance and productivity can

easily be realized.

According to the invention, there is provided a nanocarbon producing apparatus characterized by including a graphite target; a chamber which accommodates the graphite target; a window unit which  
5 is provided in a part of the chamber; a light source which irradiates light onto a surface of the graphite target through the window unit; a recovery unit which recovers a nanocarbon generated from carbon vapor, the carbon vapor being vaporized from the graphite target by the light irradiation; and a reflecting member which reflects  
10 transmitted light transmitted through the window to introduce the transmitted light to the surface of the graphite target.

In a nanocarbon producing apparatus of the invention, the optical member may include a reflecting member.

Therefore, the graphite target surface can be irradiated with  
15 the light after the optical path of the light transmitted through the window unit is changed, which allows the adhesion of the soot-like substance to the window unit to be securely suppressed.

In the invention, for example, the surface of the reflecting member can be made of metal, which preferably secures heat radiation  
20 property in the surface. Therefore, even if the soot-like substance and the like adhere to the surface, excessive rise in temperature can be suppressed. In the invention, a cooling mechanism for cooling the reflection member may further be provided. Therefore, the reflection member can be cooled more securely, which allows overheating  
25 of the reflecting member to be suppressed to improve the lifetime of the reflecting member. The nanocarbon can also stably be produced. In the invention, a cleaning mechanism for removing the soot-like

substance adhering to the reflecting member may further be provided. Therefore, the nanocarbon can be produced while removing the soot-like substance at predetermined timing, which allows the yield of the nanocarbon to be further improved.

5           In a nanocarbon producing apparatus of the invention, a shielding member located between the reflecting member and the graphite target may further be provided.

          Therefore, the window unit or the optical member can be protected more securely from the adhesion of the soot-like substance, which  
10       allows the decrease in yield of the nanocarbon to be suppressed. The lifetime of the optical member can also be lengthened.

          In a nanocarbon producing apparatus of the invention, the reflecting member may have a light focusing function. Therefore, the light can securely be focused at a predetermined position of the  
15       graphite target, which allows the nanocarbon to be stably produced. Since the light can be focused onto the graphite target surface without providing the focusing optical member to focus light, the nanocarbon can efficiently be produced with a simple configuration. The reflecting member having the light focusing function may be formed  
20       by a single member or the reflecting member may be formed by combination of the plural members.

          For example, the reflecting member can be a concave mirror. In a nanocarbon producing apparatus of the invention, the reflecting member may be a parabolic mirror. Therefore, the reflected light  
25       reflected from the concave mirror can securely be focused onto a focal point of the concave mirror. Therefore, the reflected light can be focused more securely on the surface of the graphite target, which

allows the nanocarbon to be stably produced.

In a nanocarbon producing apparatus of the invention, target holding unit which rotates the graphite target having a cylindrical shape around a central axis while holding the graphite target can  
5 be included. Therefore, the nanocarbon can continuously be produced, so that the yield of the nanocarbon can be improved.

In a nanocarbon producing apparatus of the invention, the nanocarbon may be a carbon nanohorn assembly.

Therefore, the carbon nanohorn assembly can stably be produced  
10 at high yield.

A nanocarbon producing apparatus of the invention may further have an air intake unit which generates air flow along the light traveling direction from the light source side toward the graphite target side. Therefore, the soot-like substance which is moved from  
15 the graphite target side toward the light source side to adhere to the window unit or the optical member can be suppressed more securely, which allows the lifetime of the apparatus to be lengthened more securely. The nanocarbon can also be produced more stably.

Thus, the configurations of the invention are described.  
20 However, an arbitrary combination of these configurations is also an effective aspect of the invention. Transformation of expression of the invention into another category is also an effective aspect of the invention.

As described above, according to the invention, the nanocarbon  
25 can be produced at high yield by providing the shielding member between the window unit and the graphite target. Further, according to the invention, the lifetime of the nanocarbon producing apparatus can

be lengthened.

The above and other objects, features, and advantages of the invention will be apparent from the following description of preferred embodiments and appended drawings.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

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Fig. 2 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

Fig. 3 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

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Fig. 4 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

Fig. 5 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

Fig. 6 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

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Fig. 7 is a view showing a configuration of a nanocarbon producing apparatus according to an embodiment.

Fig. 8 is a view showing a configuration of a nanocarbon producing apparatus according to Example.

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Fig. 9 is a view showing a configuration of a nanocarbon producing apparatus according to Example.

Fig. 10 is a view showing a configuration of a nanocarbon producing apparatus according to Example.

Fig. 11 is a view showing a failure time of a ZnSe window in each apparatus of Example.

Fig. 12 is a view showing a relationship between a production time and a yield of a carbon nanohorn assembly in Example.

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#### BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the invention will be described in detail below with reference to the drawings.

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(First Embodiment)

The present embodiment relates to a nanocarbon producing apparatus in which a periphery of an optical path of the light with which the surface of the graphite target is irradiated is shrouded with a cover. Fig. 1 is a sectional view showing an example of a configuration of a nanocarbon producing apparatus according to the embodiment. In this specification, Fig. 1 and other drawings used for the description of other pieces of producing apparatus are a schematic view, and the dimensions of each component do not always correspond to an actual dimension ratio.

A nanocarbon producing apparatus 125 of Fig. 1 includes a producing chamber 107, a nanocarbon recovery chamber 119, and a transportation pipe 141 which connects the producing chamber 107 and the nanocarbon recovery chamber 119. The producing apparatus of Fig. 1 also includes a laser beam source 111 which emits a laser beam 103, a ZnSe planoconvex lens 131, a ZnSe window 133, a cover 167, and a rotating device 115. The rotating device 115 holds a graphite rod

101, and the rotating device 115 rotates the graphite rod 101 about a central axis of the graphite rod 101. Further, the nanocarbon producing apparatus 125 includes an inert gas supply unit 127, a flowmeter 129, a vacuum pump 143, and a pressure gage 145.

5           In the nanocarbon producing apparatus 125, the outgoing light from the laser beam source 111 is focused by the ZnSe planoconvex lens 131, and the graphite rod 101 in the producing chamber 107 is irradiated through the ZnSe window 133 provided in a wall surface of the producing chamber 107. At this point, the laser beam 103 passes  
10 through the cover 167 provided along the optical path.

          The graphite rod 101 is used as a solid-state carbon single substance which becomes an irradiation target with the laser beam 103. The graphite rod 101 is fixed to the rotating device 115, and the graphite rod 101 can be rotated about the central axis. For  
15 example, the graphite rod 101 can be rotated such that a point irradiated with the laser beam 103 in the surface of the graphite rod 101 is separated away from a radiation direction of the laser beam 103. Specifically, in Fig. 1, the graphite rod 101 can be rotated clockwise about the central axis. Therefore, generation of optical feedback  
20 can be suppressed more securely.

          While the new surface irradiated with the laser beam 103 is stably provided, a carbon nanohorn assembly 117 can be securely recovered. The graphite rod 101 can be rotated about the central axis by fixing the graphite rod 101 to the rotating device 115. For  
25 example, the graphite rod 101 can be configured to be movable in the direction along the central axis.

          The transportation pipe 141 is communicated with the producing

chamber 107 and the nanocarbon recovery chamber 119 to connect the producing chamber 107 and the nanocarbon recovery chamber 119. The side face of the graphite rod 101 is irradiated with the laser beam 103 from the laser beam source 111. At this point, the nanocarbon recovery chamber 119 is provided toward the direction, in which a plume 109 is generated, through the transportation pipe 141. Therefore, the generated carbon nanohorn assembly 117 is recovered by the nanocarbon recovery chamber 119.

Because the plume 109 is generated in the direction perpendicular to a tangent of the graphite rod 101, that is, a normal direction at the radiation position of the laser beam 103, when the transportation pipe 141 is provided in this direction, carbon vapor can efficiently be introduced to the nanocarbon recovery chamber 119 to recover fine particles of the carbon nanohorn assembly 117. For example, when a radiation angle is set at  $45^\circ$ , the transportation pipe 141 can be provided in the direction of  $45^\circ$  relative to the normal.

In the nanocarbon producing apparatus 125, a cylindrical cover 167 with which the optical path is shrouded is provided along a passage of the laser beam 103 from the periphery of the ZnSe window 133 to the periphery of the surface of the graphite rod 101 in the producing chamber 107.. The cover 167 is provided to the periphery of the graphite rod 101, and an end portion of the cover 167 is opened. The laser beam 103 passes through the cover 167, and the surface of the graphite rod 101 is irradiated with the laser beam 103.

By providing the cover 167, the ZnSe window 133 can be shielded such that the soot-like substance, obtained from the carbon vapor generated by irradiating the surface of the graphite rod 101, does

not adhere to the ZnSe window 133 while irradiation passage of the light to the graphite rod 101 is secured. Since the soot-like substance adhesion to the surface of the ZnSe window 133 is suppressed, absorption of the laser beam 103 is suppressed in the surface of the ZnSe window 133. Therefore, the fluctuation in power density of the laser beam 103 with which the surface of the graphite rod 101 is irradiated can be suppressed. Further, excessive rise in temperature of the ZnSe window 133 can be suppressed. Therefore, the radiation position shift of the laser beam 103 due to the thermal lens effect can be suppressed in the surface of the graphite rod 101. Degradation of the ZnSe window 133 due to the overheating and the associated failure or burning can be suppressed.

Therefore, the nanocarbon producing apparatus 125 can stably produce the carbon nanohorn assembly 117 at high yield. The apparatus configuration having the excellent endurance can easily be realized.

In the nanocarbon producing apparatus 125, the transportation pipe 141 is provided along the direction in which the plume 109 is generated such that the plume 109 is shrouded. The transportation pipe 141 is communicated with the nanocarbon recovery chamber 119 provided in the lateral direction of the producing chamber 107. When the surface of the graphite rod 101 is irradiated with the laser beam 103, the plume 109 is generated, and the carbon vapor is emitted from the plume 109 to become the soot-like substance. In the nanocarbon producing apparatus 125, since the transportation pipe 141 is formed toward the direction in which the plume 109 is generated, the soot-like substance is securely introduced to the nanocarbon recovery chamber 119 through the transportation pipe 141. Therefore, recovery

efficiency of the carbon nanohorn assembly 117 can be improved. The plume 109 is generated in the direction perpendicular to the tangent of the radiation position of the laser beam 103 in the surface of the graphite rod 101.

5           The nanocarbon producing apparatus 125 has the configuration in which the side face of the graphite rod 101 is irradiated with the laser beam 103 while the graphite rod 101 is rotated in a circumferential direction. The graphite rod 101 is irradiated with the laser beam 103 in a positional relationship, in which the direction  
10 of the laser beam 103 does not coincide with the direction in which the plume 109 is generated. Therefore, the carbon nanohorn assembly 117 can efficiently be recovered at the position in which the radiation path of the laser beam 103 is intercepted.

          In the nanocarbon producing apparatus 125, the angle of the  
15 plume 109 generated in the side face of the graphite rod 101 can previously predicted, which allows the position and angle of the transportation pipe 141 to be precisely controlled. Therefore, the carbon nanohorn assembly 117 can efficiently be produced and securely be recovered on the later-mentioned conditions.

20           Then, a method of producing the carbon nanohorn assembly 117 with the nanocarbon producing apparatus 125 of Fig. 1 will specifically be described.

          In the nanocarbon producing apparatus 125, high-purity graphite, for example, rod-shaped sintered carbon or compression  
25 molded carbon can be used as the graphite rod 101.

          For example, the high-power CO<sub>2</sub> gas laser can be used as the laser beam 103. The graphite rod 101 is irradiated with the laser

beam 103 in the inert gas atmosphere using rare gas such as Ar and He, for example, at a pressure not less than  $10^3$  Pa and not more than  $10^5$  Pa. It is preferable that the inert gas atmosphere is generated after the producing chamber 107 is previously evacuated, for example,  
5 at a pressure not more than  $10^{-2}$  Pa.

It is preferable that an output, a spot diameter, and the radiation angle of the laser beam 103 are adjusted such that the power density of the laser beam 103 is substantially kept constant, for example, not less than  $5 \text{ kW/cm}^2$  and not more than  $25 \text{ kW/cm}^2$  at the  
10 side face of the graphite rod 101.

For example, the output of the laser beam 103 is set in range of not less than 1 kW and not more than 50 kW. For example, the pulse width of the laser beam 103 is set not less than 0.5 sec, and preferably not less than 0.75 sec. Therefore, cumulative energy of the laser  
15 beam 103 with which the surface of the graphite rod 101 is irradiated can sufficiently be secured, which allows the carbon nanohorn assembly 117 to be efficiently be produced. For example, the pulse width of the laser beam 103 is set not more than 1.5 sec, and preferably not more than 1.25 sec. Therefore, the decrease in yield of the carbon  
20 nanohorn assembly, caused by the fluctuation in surface energy density due to the excessive heating of the surface of the graphite rod 101, can be suppressed. It is more preferable that the pulse width of the laser beam 103 is set in the range of not less than 0.75 sec and not more than 1 sec. Therefore, both the generation rate and the  
25 yield of the carbon nanohorn assembly 117 can be improved.

For example, a quiescent width is set not less than 0.1 sec, and preferably not less than 0.25 sec. Therefore, the overheating

of the surface of the graphite rod 101 can be suppressed more securely.

The laser beam 103 irradiates such that the radiation angle is kept constant. The graphite rod 101 is rotated about the central axis at a predetermined speed while the radiation angle of the laser beam 103 is kept constant, which allows a circumferential direction of the side face of the graphite rod 101 to be continuously irradiated with the laser beam 103 at constant power density. Further, a lengthwise direction of the graphite rod 101 can continuously be irradiated with the laser beam 103 at constant power density by causing the graphite rod 101 to slide in the lengthwise direction.

In this case, it is preferable that the radiation angle ranges not less than  $30^\circ$  and not more than  $60^\circ$ . The radiation angle shall mean the angle formed between a perpendicular to the surface of the graphite target and the laser beam 103 at the radiation position of the laser beam 103. In the case of the use of the graphite rod 101 which is of the cylindrical graphite target, the radiation angle is defined by the angle formed between a horizontal plane and a line segment connecting the radiation position and the center of a circle at cross-section to be perpendicular to the length direction of graphite rod 101 .

The reflection of the laser beam 103 with which the graphite rod 101 is irradiated, namely, the generation of the optical feedback can be prevented by setting the radiation angle at least  $30^\circ$ . The generated plume 109 can also be prevented from directly striking the ZnSe planoconvex lens 131 through the ZnSe window 133. Therefore, it is effective that the ZnSe planoconvex lens 131 is protected, and it is also effective that the carbon nanohorn assembly 117 is prevented

from adhering to the ZnSe window 133. Accordingly, the power density of the laser beam 103 with which the graphite rod 101 is irradiated can be stabilized to stably produce the carbon nanohorn assembly 117 at high yield.

5           The irradiation of the graphite rod 101 with the laser beam 103 at angles not more than  $60^\circ$  enables the generation of amorphous carbon to be suppressed to improve the ratio of the carbon nanohorn assembly 117 in the product, namely, the yield of the carbon nanohorn assembly 117. It is particularly preferable that the radiation angle  
10 is set at  $45^\circ \pm 5^\circ$ . The irradiation of the graphite rod 101 with the laser beam 103 at the angle of about  $45^\circ$  can further improve the ratio of the carbon nanohorn assembly 117 in the product.

          The nanocarbon producing apparatus 125 has the configuration in which the side face of the graphite rod 101 is irradiated with  
15 the laser beam 103. Therefore, in the state in which the position of the ZnSe planoconvex lens 131 is fixed, the radiation angle relative to the side face can be changed by adjusting a height of the graphite rod 101. When the radiation angle of the laser beam 103 is changed, a radiation area of the laser beam 103 is changed in the surface of  
20 the graphite rod 101, which allows the power density to be changed. Therefore, the adjustment can securely be performed.

          Specifically, for example, in the case where the position of the ZnSe planoconvex lens 131 is fixed, the radiation angle is set at  $30^\circ$ , which allows the power density to be increased. For example,  
25 the radiation angle is set at  $60^\circ$ , which allows the power density to be controlled low.

          While the side face of the graphite rod 101 is irradiated with

the laser beam 103, the spot diameter can be set in the range of not less than 0.5 mm and not more than 5 mm.

It is preferable that the spot of the laser beam 103 is moved at a linear speed (circumferential speed) not less than 0.01 mm/sec and not more than 55 mm/sec. When the linear speed is big, the generation of the carbon vaporization from the surface of the graphite rod 101 is limited to the shallow area from the surface while the length irradiated with the laser beam 103 becomes longer at one-time pulse irradiation in the surface of the graphite rod 101 with the laser beam 103. On the contrary, when the linear speed is small, the vaporization is generated to the deep area from the surface of the graphite rod 101 while the length irradiated with the laser beam 103 becomes shorter at one-time pulse irradiation in the surface of the graphite rod 101.

It is speculated that the generation amount of the soot-like substance per unit time, that is, the generation rate of the soot-like substance and the yield of the carbon nanohorn assembly 117 in the generated soot-like substance depend on a movement distance of the radiation position and the depth of the carbon vaporization at one-time pulse light irradiation. When the carbon vaporization is excessively deep, substances other than the carbon nanohorn assembly 117 are generated to decrease the yield. When the carbon vaporization is excessively shallow, the carbon nanohorn assembly 117 is not sufficiently generated. Setting the linear speed at the above condition allows the carbon nanohorn assembly 117 to be efficiently produced at high yield.

For example, in the case where the surface of the graphite

target having the diameter of 100 mm is irradiated with the laser beam 103, the rotating device 115 rotates the graphite rod 101 having the diameter of 100 mm in the circumferential direction at a constant speed, and for example the number of revolutions is set in the range  
5 of not less than 0.01 rpm and not more than 10 rpm, which allows the above linear speed to be realized. Although the rotating direction of the graphite rod 101 is not particularly limited, it is preferable that the graphite rod 101 is rotated in the direction in which the radiation position recedes from the laser beam 103, that is, in the  
10 direction from the laser beam 103 toward the transportation pipe 141 as shown by an arrow in Fig. 1. Therefore, the carbon nanohorn assembly 117 can be recovered more securely.

The soot-like substance recovered by the nanocarbon recovery chamber 119 mainly contains the carbon nanohorn assembly 117. For  
15 example, the soot-like substance is recovered as the substance containing carbon nanohorn assembly 117 not less than 90%.

In producing the nanocarbon with the nanocarbon producing apparatus 125, the air flow may be formed along the outgoing direction of the laser beam 103 from the ZnSe window 133 to the surface of the  
20 graphite rod 101 or along the direction from the surface of the graphite rod 101 to the nanocarbon recovery chamber 119 through the transportation pipe 141. For example, the air intake unit may further be provided. The air intake unit generates the air flow along the traveling direction of the laser beam 103 from the side of the laser  
25 beam source 111 toward the side of the graphite rod 101. Therefore, the adhesion of the soot-like substance to the direction of the ZnSe window 133 from the surface of the graphite rod 101 can be suppressed

more securely. Further, because the generated carbon nanohorn assembly 117 can be introduced more securely from the transportation pipe 141 to the nanocarbon recovery chamber 119, a yield of the carbon nanohorn assembly 117 can be improved.

5           The ZnSe planoconvex lens 131 and the ZnSe window 133 are used in the nanocarbon producing apparatus 125. The ZnSe planoconvex lens may be provided as the ZnSe window 133. That is, in this case, the lens is used as the window for sealing the producing chamber 107 while the ZnSe planoconvex lens 131 is not provided outside the producing  
10   chamber 107. Therefore, the simple apparatus configuration having excellent production efficiency is realized.

In the apparatus of Fig. 1 and the pieces of apparatus described in subsequent embodiments, the laser beam source 111 is provided above the producing chamber 107. The carbon nanohorn assembly 117 generated  
15   by the irradiation with the laser beam 103 is recovered in the nanocarbon recovery chamber 119, provided in the lateral direction of the producing chamber 107, through the transportation pipe 141. In this embodiment and the subsequent embodiments, the arrangement of the laser beam source 111 is not always limited to the aspect in which  
20   the laser beam source 111 is provided above the producing chamber 107.

For example, Fig. 2 is a view showing another configuration of the nanocarbon producing apparatus having the cover 167. In the apparatus of Fig. 2, the laser beam source 111 is provided in the  
25   lateral direction of the producing chamber 107, and the laser beam 103 is emitted from the side face of the producing chamber 107 toward the graphite rod 101. At this point, the plume 109 is generated in

the direction perpendicular to the tangent of the radiation position on the graphite rod 101. In the positional relationship of Fig. 2, the plume 109 is generated toward the direction in which the angle of  $45^\circ$  is formed relative to the upward vertical direction in the producing chamber 107. In the apparatus of Fig. 2, similarly to the apparatus of Fig. 1, the transportation pipe 141 is provided from the periphery of the surface of the graphite rod 101 toward the plume generation direction, and the soot-like substance generated from the plume 109 is recovered by the nanocarbon recovery chamber 119 provided above the producing chamber 107.

In the apparatus of Fig. 2, the rotating device 115 has a rotating mechanism which holds the graphite rod 101 and rotates the graphite rod 101 about the central axis. In the apparatus of Fig. 2, similarly to the apparatus of Fig. 1, the graphite rod 101 can also be moved in the direction of the central axis.

In the apparatus of Fig. 1, the cover 167 with which the optical path is shrouded is provided along the optical path of the laser beam 103 outgoing from the laser beam source 111 as the shielding member for protecting the ZnSe window 133. However, the mode of the shielding member is not limited to the cover 167.

For example, Fig. 3 shows the apparatus having the configuration in which a partition wall 179 is provided instead of the cover 167 of the nanocarbon producing apparatus 125 of Fig. 1. Other configurations of the apparatus of Fig. 3 are similar to the nanocarbon producing apparatus 125. In the apparatus of Fig. 3, the partition wall 179 is provided in the producing chamber 107. The partition wall 179 divides the producing chamber 107 into the chamber where

the ZnSe window 133 is provided and the chamber where the graphite rod 101 is provided. A hole through which the laser beam 103 passes the graphite rod 101 is made in the partition wall 179. This enables the graphite rod 101 to be irradiated with the laser beam. The movement  
 5 of the soot-like substance generated from the graphite rod 101 side to the ZnSe window 133 side can be shielded by providing the partition wall 179. Therefore, the adhesion of the soot-like substance to the surface of the ZnSe window 133 can be suppressed.

In the pieces of apparatus of Fig. 1 to Fig. 3, the ZnSe window  
 10 133 is provided as a window in the wall surface of the producing chamber 107. However, the window is not limited to the configurations of the pieces of apparatus of Fig. 1 to Fig. 3 as long as a part of the window is exposed into the producing chamber 107. For example, the laser beam source 111 having the window in the outgoing end face may  
 15 be arranged in the producing chamber 107. In this case, the adhesion of the soot-like substance to the window of the laser beam source 111 is suppressed by shielding between the laser beam source 111 and the graphite rod 101 with the shielding member such as the cover 167 or the partition wall 179. The ZnSe planoconvex lens 131 may be  
 20 provided in the producing chamber 107. In this case, the adhesion of the soot-like substance to the surface of the ZnSe planoconvex lens 131 can be suppressed by shielding between the ZnSe planoconvex lens 131 and the graphite rod 101 with, e.g., the cover 167 or the partition wall 179 .

25

(Second Embodiment)

The present embodiment relates to a nanocarbon producing

apparatus having a configuration in which the surface of the graphite rod 101 is not directly irradiated with the light outgoing from the light source 111, but the surface of the graphite rod 101 is irradiated after the light is reflected to change the optical path.

5            Fig. 4 is a sectional view showing a state of a nanocarbon producing apparatus 173 according to the embodiment when laterally viewed. In the embodiment, the same component as the nanocarbon producing apparatus 125 described in the first embodiment is designated by the same reference numeral, and the description will be neglected  
10 as appropriate.

          In the configuration of the nanocarbon producing apparatus 125 (Fig. 1), after the laser beam 103 outgoing from the laser beam source 111 is focused by the ZnSe planoconvex lens 131 such that the spot diameter becomes a predetermined size in the surface of the  
15 graphite rod 101, the laser beam 103 irradiates the producing chamber 107 through the ZnSe window 133. On the other hand, in the nanocarbon producing apparatus 173 of Fig. 4, the laser beam 103 irradiates the producing chamber 107 through the ZnSe window 133 with the laser beam 103 outgoing from the laser beam source 111 while the laser beam 103  
20 is not focused. Because the nanocarbon producing apparatus 173 has a plane mirror 169 and a parabolic mirror 171 to change the optical path of the laser beam 103, the laser beam 103 is reflected by the plane mirror 169 and further reflected by the parabolic mirror 171 in the producing chamber 107. The light reflected from the parabolic  
25 mirror 171 is focused onto the surface of the graphite rod 101 placed near the focal point of the parabolic mirror 171.

          Thus, in the nanocarbon producing apparatus 173, the surface

of the graphite rod 101 is not directly irradiated with the laser beam 103 incident into the producing chamber 107 through the ZnSe window 133, but the surface of the graphite rod 101 is irradiated after the optical path is changed by twice of reflection with the plane mirror 169 and the parabolic mirror 171. Since the laser beam 103 passes through the plane mirror 169 and the parabolic mirror 171, the length of the optical path from the ZnSe window 133 to the graphite rod 101 can be increased in the nanocarbon producing apparatus 173 when compared with the nanocarbon producing apparatus 125.

Therefore, the nanocarbon producing apparatus 173 has the configuration, in which the adhesion of the plume 109 generated from the surface of the graphite rod 101 to the ZnSe window 133 and the adhesion of the soot-like substance obtained from the plume 109 to the ZnSe window 133 are suppressed. Accordingly, even if the nanocarbon producing apparatus 173 is used for a long period, the change in power density of the laser beam 103 with which the surface of the graphite rod 101 is irradiated can be suppressed. As a result, the decrease in yield of the carbon nanohorn assembly 117 can be suppressed, and the continuous production of the carbon nanohorn assembly 117 can stably be performed. Further, the lifetime of the nanocarbon producing apparatus 173 can be lengthened.

In the nanocarbon producing apparatus 173, for example, Cu can be used as the material of the plane mirror 169 or the parabolic mirror 171. Since Cu has high thermal conductivity, even if the soot-like substance adheres to the surface, the heat is efficiently radiated. In the plane mirror 169 and the parabolic mirror 171, the surface is coated with, e.g., Au or Mo. The failure of the plane

mirror 169 or the parabolic mirror 171 can be suppressed by using these materials.

In the nanocarbon producing apparatus 173, after the light outgoing from the laser beam source 111 is reflected twice, the surface of the graphite rod 101 is irradiated with the light. However, as long as the light reaches the surface of the graphite rod 101 after changing the optical path of the light outgoing from the laser beam source 111, the number of reflection times is not particularly limited. The nanocarbon producing apparatus 173 may be configured to perform the one-time reflection, or irradiate the graphite rod 101 after the reflection of not less than three times.

In the configuration of the nanocarbon producing apparatus 173, the laser beam 103 is focused onto the surface of the graphite rod 101 by reflecting the laser beam 103 with the parabolic mirror 171. However, as long as the laser beam 103 is configured to be able to be focused on the surface of the graphite rod 101, the shape of the reflecting mirror is not limited to the parabolic mirror 171. For example, a concave mirror having another shape can be used. The laser beam 103 may be focused on the surface of the graphite rod 101 by the combination of the plural reflecting mirrors.

#### (Third Embodiment)

The present embodiment relates to another configuration of a nanocarbon producing apparatus. In the embodiment, the same component as the nanocarbon producing apparatus 125 (Fig. 1) described in the first embodiment or the nanocarbon producing apparatus 173 (Fig. 4) described in the second embodiment is designated by the same

reference numeral, and the explanation will not be described as appropriate.

Fig. 5 is a sectional view showing a state of a nanocarbon producing apparatus 175 according to the embodiment when laterally viewed. The basic apparatus configuration of the nanocarbon producing apparatus 175 is similar to the nanocarbon producing apparatus 173 (Fig. 4). However, the nanocarbon producing apparatus 175 differs from the nanocarbon producing apparatus 173 in that the cover 167 for protecting the passage of the laser beam 103 is provided.

As described in the first embodiment, the direct adhesion of the soot-like substance, generated from the plume 109, to the ZnSe window 133 can be suppressed more securely by providing the cover 167. The adhesion of the soot-like substance to the surface of the plane mirror 169 or the parabolic mirror 171 can also be prevented more securely. Therefore, the fluctuation in radiation position of the laser beam 103 or the fluctuation in power density of the laser beam 103 is suppressed in the surface of the graphite rod 101, which suppresses the decrease in yield of the carbon nanohorn assembly 117. Further, the apparatus lifetime can further be lengthened.

In the nanocarbon producing apparatus 175 of Fig. 5, since the cover 167 is provided while being in contact with the wall surface of the producing chamber 107, the ZnSe window 133 is provided inside the producing chamber 107. However, as long as the nanocarbon producing apparatus is configured to seal the inert gas in the producing chamber 107, the position of the ZnSe window 133 is not limited to the inside of the producing chamber 107. For example, the ZnSe window 133 may be provided in the wall surface of the producing chamber 107.

For example, Fig. 6 is a view showing a nanocarbon producing apparatus 176 in which the ZnSe window 133 is provided in the wall surface of the producing chamber 107.

5 (Fourth Embodiment)

In the above embodiments, the case in which the graphite rod is used is described by way of example. However, in any one of the above embodiments, the shape of the graphite target is not limited to the cylindrical shape. For example, the graphite target may be  
10 formed in sheet-like or rod-shaped and the like.

For example, Fig. 7 is a view showing the apparatus configuration in the case where the sheet-like graphite target is used in the nanocarbon producing apparatus 175 (Fig. 5) described in the third embodiment.

15 In a nanocarbon producing apparatus 177 of Fig. 7, a graphite target 139 is the solid-state carbon single substance which becomes the target irradiated with the laser beam 103. The graphite target 139 is held by a target holding unit 153 on a target supply plate 135. A plate holding unit 137 horizontally moves the target supply  
20 plate 135 in a translational manner. Therefore, when the target supply plate 135 is moved, the graphite target 139 placed thereon is also moved, which allows the radiation position of the laser beam 103 and the surface of the graphite target 139 to be relatively moved.

For example, screw threads are formed in a bottom surface of  
25 the target supply plate 135 and the surface of the plate holding unit 137, and the target supply plate 135 can be moved in the direction from the upper left toward the lower right of Fig. 7 in a rack and

pinion manner. A groove (not shown) or the like is formed in the surface of the target supply plate 135, a projection (not shown) is formed in the bottom portion of the target holding unit 153 so as to slide the groove, and the projection is set in the groove.

5 Therefore, the graphite target 139 held by the target holding unit 153 and the target holding unit 153 can be moved in the direction perpendicular to the sheet plane of Fig. 7.

This configuration enables the graphite target 139 to be supplied to the radiation position of the laser beam 103 outgoing  
10 from the laser beam source 111.

When the graphite target is formed in sheet-like or rod shaped, a thickness of the graphite target is formed to an extent in which the graphite target is completely vaporized and run out when the graphite target is irradiated with the laser beam 103 once or several  
15 times. Therefore, the yield of the carbon nanohorn assembly 117 can further be improved. When the graphite target is irradiated with the laser beam 103 once, the surface of the graphite rod 101 is roughened, which causes the fluctuation of power density in irradiating the graphite rod 101 with the laser beam 103 again. Therefore, the carbon  
20 nanohorn assembly 117 can stably be produced as the number of irradiation times of the surface of the graphite rod 101 with the laser beam 103 is decreased.

Thus, the invention is described based on the embodiments. Those skilled in the art will understand that these embodiments are  
25 illustrated by way of example only, various modifications could be made, and the modifications are also included in the scope of the invention.

In the configurations of the pieces of apparatus according to the above embodiments, the soot-like substance obtained by irradiating the graphite target with the laser beam 103 is recovered by the nanocarbon recovery chamber 119. However, the soot-like substance can be recovered by depositing on a proper substrate, or the soot-like substance can be recovered by the method of recovering fine particles with a dust bag. The inert gas can also be circulated in the reaction chamber to recover the soot-like substance by the flow of the inert gas.

10 In the above embodiments, when the carbon nanohorn assembly 117 is produced, the conditions such as the power density, the pulse width, and the quiescent width of the laser beam on the graphite target surface and the moving speed of the graphite target can be appropriately selected according to the shape of the graphite target or the shape of the target carbon nanohorn assembly 117. The shape, the diameter, 15 the length, the shape of a leading end portion of the carbon nanohorn constituting the carbon nanohorn assembly 117, a distance between carbon molecules or the carbon nanohorns, and the like can be variously controlled by the irradiation condition of the laser beam 103 and 20 the like.

In the pieces of apparatus shown in the second to fourth embodiments (Fig. 4 to Fig. 7), the ZnSe window 133 is provided as the window in the wall surface of the producing chamber 107. However, the window is not limited to the configurations of the second to fourth 25 embodiments as long as a part of the window is exposed into the producing chamber 107. For example, the laser beam source 111 having the window in the outgoing end face may be arranged in the producing chamber

107. In this case, the adhesion of the soot-like substance to the window of the laser beam source 111 is suppressed by causing the light outgoing from the laser beam source 111 to reach the surface of the graphite rod 101 after the light is reflected from the reflecting mirror such as the plane mirror 169 and the parabolic mirror 171. The ZnSe planoconvex lens 131 may be provided in the producing chamber 107. In this case, the adhesion of the soot-like substance to the surface of the ZnSe planoconvex lens 131 can be suppressed by causing the light transmitted through the ZnSe planoconvex lens 131 to reach the surface of the graphite rod 101 after the light is reflected from the reflecting mirror such as the plane mirror 169 and the parabolic mirror 171.

In the pieces of apparatus shown in the second to fourth embodiments (Fig. 4 to Fig. 7), the cooling mechanism for cooling the parabolic mirror 171 may further be provided. Since the excessive heating is suppressed by cooling the parabolic mirror 171 even if the soot-like substance adheres to the surface of the parabolic mirror 171, the apparatus lifetime can further be lengthened. The cleaning mechanism for removing the soot-like substance adhering to the surface of the parabolic mirror 171 may be provided. Therefore, since the soot-like substance can be removed at predetermined timing even if the soot-like substance adheres to the surface of the parabolic mirror 171, the control can be performed more securely such that the power density of the light with which the surface of the graphite rod 101 is irradiated is kept constant. Accordingly, the yield of the carbon nanohorn assembly can further be improved. Further, the apparatus lifetime can further be lengthened. In this case, the parabolic mirror

171 is described as examples of the cooling mechanism and the cleaning mechanism. In addition, these mechanisms can be provided to the plane mirror 169 if needed.

The invention will further be described based on Example.

5 However, the invention is not limited to the following Example.

(Example)

In Example, the carbon nanohorn assembly 117 was produced by the laser ablation method using the nanocarbon producing apparatus 126 shown in Fig. 2 and the pieces of nanocarbon producing apparatus shown in Fig. 8, Fig. 9, and Fig. 10. However, in the nanocarbon producing apparatus 173 shown in Fig. 4 and the nanocarbon producing apparatus 175 shown in Fig. 5, the pieces of apparatus of Fig. 8 and Fig. 9 have the configuration in which the laser beam 103 is incident from the side face of the producing chamber 107 like the nanocarbon producing apparatus 126. The nanocarbon producing apparatus of Fig. 10 has the configuration similar to the nanocarbon producing apparatus 126 of Fig. 2, and differs from the nanocarbon producing apparatus 126 in that the nanocarbon producing apparatus of Fig. 10 does not have the cover 167.

The rod-shaped sintered carbon having the diameter of 100 mm was used as the solid-state carbon substance. The rod-shaped sintered carbon was placed in the vacuum chamber. After the chamber was evacuated up to  $10^{-2}$  Pa, the Ar gas was introduced such that the atmospheric pressure became  $1.01325 \times 10^5$  Pa. Then, the solid-state carbon substance was irradiated with the high-output CO<sub>2</sub> laser beam at room temperature. The laser output was set at 100 W, and the power

density was set at  $22 \text{ kW/cm}^2$  in the surface of the solid-state carbon substance. The pulse width was set at 1 sec, and the quiescent width was set at 250 msec. While the solid-state carbon substance was rotated at 6 rpm, the surface of the solid-state carbon substance was irradiated with the laser beam such that the radiation angle was set at  $45^\circ$ . The laser beam irradiation was performed until the ZnSe window failed, and the time for the ZnSe window to fail was measured in each apparatus.

Further, in the case where the apparatus of Fig. 10 and the nanocarbon producing apparatus 173 of Fig. 8 were used, a relationship between a production time and the yield of the carbon nanohorn assembly 117 was studied.

Fig. 11 is a view showing a failure time of the ZnSe window in each apparatus. Referring to Fig. 11, "ZnSe" is the experimental result for the apparatus of Fig. 10. "ZnSe + nanocarbon adhesion prevention corn", "parabolic mirror", and "parabolic mirror + nanocarbon adhesion prevention corn" indicate the experimental results for the nanocarbon producing apparatus shown in Fig. 2, Fig. 8, and Fig. 9 respectively.

From Fig. 11, in the apparatus configuration in which the light beam was focused with the ZnSe planoconvex lens 131, it was clear that an endurance time of the ZnSe window 133 was increased by providing the cover 167. It was clear that the endurance time of the ZnSe window 133 was remarkably increased by the configuration in which the light beam was focused with the parabolic mirror 171, and the endurance time of the ZnSe window 133 was increased by further providing the cover 167.

From this result, it was confirmed that the apparatus lifetime

was able to be lengthened by the configuration in which the surface of the graphite rod 101 was irradiated with the laser beam 103 after reflecting and focusing the laser beam 103 with the parabolic mirror 171.

5            Fig. 12 is a view showing the relationship between a production time and the yield of the carbon nanohorn assembly 117 for the pieces of apparatus of "ZnSe" and "parabolic mirror" in Fig. 11, namely, for the pieces of apparatus of Fig. 10 and Fig. 8. As can be seen from Fig. 12, in the apparatus of Fig. 10, the yield of the carbon  
10 nanohorn assembly 117 is decreased as the production time passes. On the contrary, in the case where the nanocarbon producing apparatus 173 of Fig. 8 is used, even if the production time is lengthened, it is found that the yield of the carbon nanohorn assembly 117 is not decreased and the yield is kept constant. Therefore, it was clear  
15 that the carbon nanohorn assembly was able to be stably produced at high yield by reflecting the laser beam 103 with the plane mirror 169 and the parabolic mirror 171, or by focusing the laser beam 103 onto the surface of the graphite rod 101 with the parabolic mirror 171.